UNIVERSITY OF PENNSYLVANIA

THE POLYMERIC STATES AND THE STRUCTURES OF METHYLENE-ANILINE AND METHYLENE-PARA-TOLUIDINE. THE CONDENSATION OF ANILINE AND ACETALDEHYDE

JOHN GEORGE MILLER

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA

1932

THE POLYMERIC STATES AND THE STRUCTURES OF METHYLENE-ANILINE AND METHYLENE-PARA-TOLUIDINE. THE CONDENSATION OF ANILINE AND ACETALDEHYDE

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

JOHN GEORGE MILLER

Reprint from
The Journal of the American Chemical Society, Vol. 54, No. 9

PHILADELPHIA
1932

ACKNOWLEDGMENT

The author expresses his sincere appreciation of the inspiration and guidance of Dr. E. C. Wagner, who suggested the subject of the problem and continually aided its solution.

R. UNIV.
BIBLIOTHEEK
LEIDEN

THE POLYMERIC STATES AND THE STRUCTURES OF METHYLENE-ANILINE AND METHYLENE-PARA-TOLUIDINE. THE CONDENSATION OF ANILINE AND ACETALDEHYDE

By John G. Miller

N-Methylene-aniline and N-methylene-*p*-toluidine are Schiff bases which have been obtained only in polymerized forms.[1] Published evidence as to their polymeric states is in part conflicting,[1d,2] and that as to their structures is scanty and unconvincing.[1a,b,2,3]

Methylene-aniline has long been recognized as trimeric. Methylene-*p*-toluidine, stated by Bischoff[1d] to be trimeric, was later reported by Ingold and Piggott[2] to be dimeric at ordinary temperature, a finding shown below to be incorrect. Though the degree of polymerization is affected by conditions such as temperature and presence of the bases in hot solvents, the polymers referred to here, when perfectly pure, are relatively stable under

[1] (a) Wellington and Tollens, *Ber.*, **18**, 3298 (1885); (b) Miller and Plöchl, *ibid.*, **25**, 2020 (1892); (c) Pulvermacher, *ibid.*, **25**, 2762 (1892); (d) Bischoff, *ibid.*, **31**, 3248 (1898).

[2] Ingold and Piggott, *J. Chem. Soc.*, **123**, 2745 (1923).

[3] (a) Pratesi, *Gazz. chim. ital.*, **14**, 351 (1884); (b) Tröger, *J. prakt. Chem.*, [2] **35**, 225 (1887); (c) Grünhagen, *Ann.*, **256**, 285 (1890); (d) Eibner, *ibid.*, **302**, 349 (1898); (e) Löb, *Z. Elektrochem.*, **4**, 428 (1898); (f) Goecke, *ibid.*, **9**, 470 (1903).

ordinary conditions, and have the characteristics of definite compounds.

Ring structures were assigned to polymerized methylene-aniline and methylene-*p*-toluidine by Bischoff, on the basis of analytic and molecular weight values.[1d,4] Löb,[3e] by electro-reduction of *p*-nitrotoluene in acid solution containing formaldehyde, obtained dimethyl-*p*-toluidine, whose formation was interpreted as evidence for the ring structure of the presumably intermediate methylene-*p*-toluidine, some of which appeared as a product.

Ingold and associates,[5] as a result of experiments on the thermal "division" of certain coupled azomethines, stated them to be compounds containing the 1,3-dimethinediazidine ring, and Ingold and Piggott[2] concluded that methylene-*p*-toluidine is a stable example of this type, *i. e.*, a cyclic dimer. The validity of these conclusions hinges upon the molecular weight of methylene-*p*-toluidine, for which a single value 254 was reported, that calculated for the dimer being 238. In the present study, however, the molecular weight of methylene-*p*-toluidine was found, by cryoscopic determinations in four solvents, to be 353, that calculated for the trimer being 357. Ingold and Piggott's representation of methylene-*p*-toluidine as N,N′-bis-(*p*-tolyl)-1,3-dimethinediazidine is therefore inadmissible. The successful extension, to methylene-aniline and methylene-*p*-toluidine, of the method of structure proof used by Wagner[6] in the case of methylene-*p*-aminophenol is described below.

The Polymeric States of Methylene-aniline and Methylene-*p*-toluidine.—Pure methylene-aniline (m. p. 141.2° corr.) was shown, by cryoscopic determinations in benzene, nitrobenzene, ethylene bromide and 1,4-dioxane (temperatures 5 to 12°), to be definitely trimeric, the results of fourteen concordant values averaging 320; the calculated value for the trimer is 315. In boiling benzene the result was likewise 320, but in molten camphor the value obtained was 255, indicating partial depolymerization at 176°.

The amorphous "higher polymeride" of methylene-aniline (decomp. above 210°), stated by Bischoff to be approximately tetrameric in boiling benzene, was found to have in molten camphor the molecular weight 254, identical with that of initially trimeric methylene-aniline under the same conditions; the agreement suggests that this value may represent the average polymeric state at 176°.

Pure methylene-*p*-toluidine (m. p. 127.9° corr.) was found, as already noted, to be definitely trimeric when examined cryoscopically in benzene,

[4] Synthetic evidence of ring structure was obtained by Grünhagen[3c] and by Eibner (Ref. 4d, p. 355), but the indications were actually somewhat misleading.

[5] Ingold and Piggott, *J. Chem. Soc.*, **121**, 2381, 2793 (1922); Ingold, *ibid.*, **125**, 87 (1924); **127**, 1141 (1926); Ingold and Shoppee, *ibid.*, 1199 (1929).

[6] Wagner, *J. Am. Chem. Soc.*, **54**, 660 (1932).

nitrobenzene, ethylene bromide and 1,4-dioxane, sixteen results averaging 353. In boiling benzene the value was 338 (trimeric), but in molten camphor it was 213, *i. e.*, about 11% below the molecular weight of the dimer. Ingold and Piggott reported this compound to be monomeric at 250° (Victor Meyer method).

The amorphous "higher polymeride" of methylene-*p*-toluidine (m. p. 225–227°), reported by Bischoff to be approximately tetrameric in boiling benzene, was found to have at 176° (in molten camphor) the molecular weight 249, or 5% above that of the dimer.

The slight solubilities of the two higher polymers in cold benzene, etc., prevented determination of their molecular weights at lower temperatures. Collected results of the molecular weight determinations of methylene-aniline and methylene-*p*-toluidine are given in Table I.

The Reduction of Methylene-aniline and of Methylene-*p*-toluidine.—The trimeric bases, and also their higher polymerides, were reduced by zinc dust and concentrated hydrochloric acid at 5–10°, this temperature being presumably favorable to the stability of the several polymers. The maximum extent of hydrolysis under the same conditions was independently determined by recovery of the aniline or *p*-toluidine produced.

Reduction of trimeric methylene-aniline and of its amorphous higher polymeride yielded aniline (in excess of that attributable to hydrolysis), methylaniline and dimethylaniline. In the procedure developed for the separation and estimation of these products,[7] dimethylaniline was precipitated as the hydroferrocyanide,[8] aniline as the zincichloride,[9] and finally methylaniline as the benzenesulfonyl derivative. The usefulness of this separation was established by both qualitative and quantitative tests using mixtures of known composition.

Reduction of trimeric methylene-*p*-toluidine and of its amorphous higher polymeride was almost quantitative, and yielded *p*-toluidine (in excess of that attributable to hydrolysis), methyl-*p*-toluidine, and dimethyl-*p*-toluidine. The primary and secondary bases were separated and estimated as their benzenesulfonyl derivatives by the Hinsberg–Kessler procedure,[10] and dimethyl-*p*-toluidine as its nearly insoluble

[7] The Hinsberg–Kessler method was found to be unsatisfactory due to interaction of the reagent with dimethylaniline to form a blue dye [Hassencamp, *Ber.*, **12**, 1275 (1879); Michler and Meyer, *ibid.*, **12**, 1791 (1879); Wahl, *Rev. gen. mat. color.*, **32**, 176 (1928); *Chem. Abstracts*, **23**, 1896 (1929)].

[8] Fischer, *Ann.*, **190**, 184 (1878); Eisenberg, *ibid.*, **205**, 265 (1880); Beckmann and Correns, *Ber.*, **55**, 854 (1922).

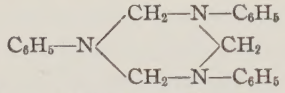
[9] Lachowicz and Bandrowski, *Monatsh.*, **9**, 510 (1888) Frankland, Challenger and Nicholls, *J. Chem. Soc.*, **115**, 198 (1919).

[10] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. II, 1916, p. 24.

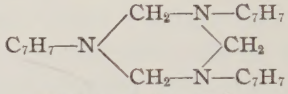
picrate. Tests of this method of separation showed its accuracy to approach the quantitative.

Results of reduction and hydrolysis experiments conducted semi-quantitatively are given in Table II.

The Structures of Methylene-aniline and Methylene-*p*-toluidine.—The formation of primary, secondary and tertiary amines, all as major reduction products of methylene-aniline and methylene-*p*-toluidine (both the trimeric and the higher forms), constitutes evidence as to structure. The appearance of the dimethylated bases is perhaps of most significance, as it indicates the original molecule to contain nitrogen attached to two methylene groups. As, furthermore, crystalline methylene-aniline and methylene-*p*-toluidine are shown conclusively to be trimeric within the range 5 to 80°, there is thus available the first definite evidence that these compounds have cyclic structures



Methylene-aniline,
M. p. 141.2° corr.



Methylene-*p*-toluidine,
M. p. 127.9° corr.

Equally definite conclusions cannot be reached for the amorphous higher polymers, due to ignorance of their molecular weights at lower temperatures. The evidence of reduction admits the possibility of rings, ring-aggregates or (if the molecular weights are large) of indeterminate chain structures of the Staudinger[11] type

$$\ldots.CH_2NCH_2NCH_2NCH_2N\ldots.$$
$$\quad\quad Ar \quad Ar \quad Ar \quad Ar$$

The Condensation of Aniline and Acetaldehyde.—Condensations of aniline with lower normal aliphatic aldehydes other than formaldehyde[12] were shown by Miller and Plöchl and their students[1b] to yield in each case as one product an oil stated to be the simple azomethine $C_6H_5N{=}CHR$, which changed into a dimeric molecule represented, *e. g.*, $C_6H_5NHCH(CH_3)CH_2CH{=}NC_6H_5$, due to an aldol-like condensation.[13] The "polymerization" of the azomethines $C_6H_5N{=}CHR$ was thus indicated to be entirely different from that of the azomethines $ArN{=}CH_2$ from formaldehyde. In the present study the reaction of acetaldehyde with aniline was examined to determine whether the monomeric azomethine could be isolated, and whether it might not polymerize after the manner of methylene-aniline and methylene-*p*-toluidine.

[11] Staudinger, *Ber.*, **59**, 3019 (1926).

[12] For the behavior of isobutyraldehyde and isovaleraldehyde see Friedjung and Mossler, *Monatsh.*, **22**, 460 (1901); Eibner and Purucker, *Ber.*, **33**, 3658 (1900).

[13] Eibner, *Ber.*, **27**, 1281 (1894); **29**, 2977 (1896); *Ann.*, **318**, 58 (1901); **328**, 121 (1903). Eibner obtained the above compound by condensation of aldol and aniline. See also Strain, *J. Am. Chem. Soc.*, **54**, 1221 (1932).

Condensations of aniline and impure acetaldehyde, especially if effected without continued cooling, yielded oily and colored products such as those mentioned. When both reactants were pure, and were condensed with chilling, the product was a white crystalline solid found to be ethylidene-dianiline $(C_6H_5NH)_2CHCH_3$, previously prepared by Eibner.[14] Efforts to force azomethine formation by use of acetaldehyde in excess were unsuccessful, the product being in every case the di-imine. This tendency of straight-chain aliphatic aldehydes to yield di-imines had been observed by Eibner.[15] Ethylidene-dianiline appeared to be stable only in the cold; on standing at room temperature it liquefied and became colored, presumably with gradual conversion to the "dimer."

Acetaldehyde and aniline therefore appear to yield no isolable azomethine, either as the monomer or a true polymer. The "dimers" of Miller and Plöchl are probably products formed by secondary changes.

Experimental

Chemicals.—The formaldehyde was Baker's "C. P." grade (35%). The acetaldehyde (Coleman and Bell "C. P.") was distilled through a column, only the portion boiling constant at 20.8° being taken. The other chemicals were the best Eastman Kodak Company grades, purified as follows. Aniline was redistilled from zinc dust under reduced pressure. Methylaniline and dimethylaniline were redistilled under reduced pressure. Methyl-*p*-toluidine and dimethyl-*p*-toluidine were fractionally distilled. Ethylaniline was freed from traces of diethylaniline by hydrolysis of the recrystallized acetyl compound of m. p. 54°, and the recovered base dried and distilled. Benzenesulfonyl chloride was distilled *in vacuo*. The molecular weight solvents benzene, nitrobenzene, ethylene bromide and 1,4-dioxane were purified by partial freezings of the redistilled compounds, and camphor by sublimation.

Preparation and Purification of the Schiff Bases Studied

Methylene-aniline (Trimeric).—A mixture of aniline with ten parts of water was chilled, and a slight excess of formalin added with stirring. The precipitated product was filtered off the next day, and dried *in vacuo*. To purify, it was extracted rapidly with about five parts of boiling alcohol, the extract filtered quickly, and the filtrate chilled at once with stirring, some water being added gradually to hasten the separation and decrease the conversion of the trimer to the higher polymer. The product melted at 140° with slight opacity (trace of higher polymer), and was considered satisfactory for the reduction experiments. For molecular weight determinations it was recrystallized from hot 95% alcohol, or better from 60–80° ligroin, working rapidly, and filtering off the crystals which separated immediately upon chilling. Recrystallization from benzene was found unsatisfactory due to invariable formation of the higher polymer.

Pure methylene-aniline was obtained as thin transparent prisms, showing oblique extinction, and melting sharply to a clear liquid at 139.5° (141.2° corr.). It distilled apparently without change *in vacuo* (60–64° at 29 mm.).

Amorphous methylene-aniline (the higher polymer) was accumulated in small portions as a by-product of recrystallizations of the trimer, and was freed from trimer by extraction with benzene. It was also made from crude methylene-aniline by re-

[14] Eibner, *Ber.*, **30**, 1444 (1897).

[15] Eibner, *Ann.*, **302**, 349 (1898); **316**, 89 (1901); **328**, 121 (1903).

peatedly boiling it with benzene and then extracting with hot ligroin. It was obtained as a white powder, without crystalline structure or optical activity. It decomposed above 210° without melting, and was almost insoluble in hot benzene, ligroin, alcohol, etc.

Methylene-*p*-toluidine (Trimeric).—A solution of *p*-toluidine in six parts of 95% alcohol was chilled, vigorously stirred, and an excess (two equivalents) of formalin added all at one time. After thirty minutes the mass of crystals was filtered off, washed with cold alcohol, and dried *in vacuo;* the yield was 90%. To purify, it was extracted rapidly with hot ligroin (60–80°) and the extract filtered quickly; the higher polymer remained on the filter. The filtrate was cooled rapidly, but only to room temperature, so as to retain any di-imine in solution. The crystals were washed with cold ligroin.

Pure trimeric methylene-*p*-toluidine was obtained as silky needles, showing oblique extinction, and melting sharply to a clear liquid at 127° (127.9° corr.); it was distillable *in vacuo.*

Amorphous methylene-*p*-toluidine (the higher polymer) was obtained in small portions as a by-product as mentioned above. It was prepared in 59% yield by condensing *p*-toluidine and excess formaldehyde in alcohol, and then warming the well-stirred mixture to 50–60° in the water-bath. The insoluble product was extracted three times with boiling ligroin to remove any trimer. The higher polymer was a white amorphous powder, without optical activity, and practically insoluble in the solvents used. It melted at 225–227° with decomposition.

Ethylidene-dianiline.—An ice-chilled solution of pure acetaldehyde in 60 parts of water was treated with one equivalent of aniline. After some minutes the liquid was decanted from the white granular precipitate, which was washed with ice water five times by decantation. The product, collected in an ice-jacketed filter and dried *in vacuo* in an ice-chilled "pistol" in presence of "desicchlora," melted at 49°; this and the results of reduction (see later) identified it as ethylidene-dianiline. The same product resulted when an excess of aldehyde (up to two equivalents) was used. As mentioned above, this compound became oily and colored on standing at room temperature; similar colored oils were obtained by cold condensation of ordinary (not purified) aniline and acetaldehyde.

Molecular Weight Determinations.—The two Beckmann thermometers used were certified by the Bureau of Standards. For molecular weights by the Rast method there was used an untested "turpentine thermometer" graduated from 145 to 200° in 0.2°. Ebullioscopic measurements were made using the Cottrell apparatus. To determine the concentration of the solute an aliquot was removed and the solvent evaporated; the bases thus recovered were found to have undergone partial conversion to the higher polymers. Results of molecular weight determinations are collected in Table I.

Reduction and Hydrolysis Experiments

The general reduction procedure was as follows. An intimate mixture of the Schiff base with about twice its weight of zinc dust was added in small portions to 15 parts of concentrated hydrochloric acid initially at 0° and chilled thereafter in an ice-bath. Reduction proceeded smoothly, without frothing, and yielded finally a clear solution. The liquid was made alkaline and steam distilled. The distillate was extracted with ether, the extract dried with sodium sulfate, filtered into a tared beaker, the ether evaporated, and the residue of mixed bases weighed and then treated to separate the individual components, as outlined in the following examples. In the semi-quantitative experiments the precipitates were collected in glass filter crucibles, suitably washed and dried, and weighed.

Methylene-aniline.—The mixed bases were dissolved in the least amount of 6 *N* hydrochloric acid and treated in the cold with strong potassium ferrocyanide solution. The precipitated dimethylaniline-hydroferrocyanide was washed with cold water

TABLE I

MOLECULAR WEIGHT DETERMINATIONS FOR METHYLENE-ANILINE AND METHYLENE-*p*-TOLUIDINE

Methylene-aniline m. p. 141.2°	Methylene-*p*-toluidine m. p. 127.9°	Methylene-aniline m. p. 141.2°	Methylene-*p*-toluidine m. p. 127.9°
Benzene (cryoscopic)		1,4-Dioxane (cryoscopic)	
318	352	312	385
334	349	307	338
	356	319	348
	355	315	370
	350		
		Benzene (ebullioscopic)	
Nitrobenzene (cryoscopic)		322	302
312	328	300	385
303	337	308	328
317	326	350	
309			
		Camphor (cryoscopic)	
Ethylene bromide (cryoscopic)		264	209
318	375	245	217
325	363		
338	375	Higher polymer m. p. above 210°	Higher polymer m. p. 225–227°
333	371	261	249
		246	249

and alcohol, and dried at 80°. The base was identified by conversion to *p*-nitrosodimethylaniline, m. p. 85°. The filtrate was made alkaline, extracted with ether, the ether evaporated and the chilled residue treated with excess of strong zinc chloride solution (containing only enough hydrochloric acid to keep it clear). The aniline zinc chloride was washed with ligroin and dried at 80°. A little more aniline was recovered later, as noted below. The filtrate was made alkaline, extracted with ether, the ether evaporated and the residual oil dissolved in dilute hydrochloric acid. The solution was made strongly alkaline and was shaken with an excess of benzenesulfonyl chloride. The precipitated benzenesulfonyl derivative of methylaniline (blue-tinted due to a trace of dimethylaniline) was filtered off, washed, and dried *in vacuo*. After crystallization from alcohol it melted at 76–77° uncorr. The alkaline filtrate on acidification yielded a further small quantity of aniline as the benzenesulfonyl derivative (m. p. 110–111° uncorr.).

Methylene-*p*-toluidine.—The mixed bases obtained by reduction were shaken in the cold with aqueous sodium hydroxide and benzenesulfonyl chloride, the mixture was finally acidified, and the benzenesulfonyl derivatives extracted in ether. The aqueous liquid was made alkaline and extracted with ether. The solvent was evaporated, the residual oil dissolved in dilute acetic acid, and dimethyl-*p*-toluidine precipitated and weighed as the picrate, which, after recrystallization from alcohol, melted at 129° uncorr. The ether solution of the mixed benzenesulfonyl derivatives was shaken with dilute sodium hydroxide. The aqueous layer was acidified, chilled, and the precipitated benzenesulfonyl derivative of *p*-toluidine filtered off, washed and dried at 80°; it melted at 120°. The ether layer was evaporated, and the residue refluxed with sodium alcoholate. The liquid was diluted with water, the alcohol evaporated, and the N-(methyl-*p*-tolyl)-benzenesulfonamide filtered off; it melted at 65° uncorr. The filtrate on acidification yielded a little more N-(*p*-tolyl)-benzenesulfonamide.

The *extent of hydrolysis* of methylene-aniline and methylene-*p*-toluidine by acid

was tested by the procedure used for reduction, with omission of the zinc. The steam-volatile oils were found to consist of aniline and *p*-toluidine, respectively (no secondary or tertiary bases), which were determined as in the reduction experiments. That the hydrolysis occurred during the contact with acid and not during the steam distillation in presence of alkali was shown by experiments made to test the latter possibility, no steam-volatile products being obtained.

Results of reduction and hydrolysis experiments appear in Table II.

TABLE II

REDUCTION AND HYDROLYSIS OF METHYLENE-ANILINE AND METHYLENE-*p*-TOLUIDINE[a]

	Methylene-aniline				Methylene-*p*-toluidine			
Experiment	Taken g.	Aniline %	Methyl-aniline %	Di-methyl-aniline %	Taken g.	Toluidine %	Methyl-toluidine %	Di-methyl-toluidine %
Test of sepn. of 1, 2 and 3° amines	[b]	96.7	66.6	85.1	[c]	98.4	102.7	95.9
Hydr. of trimer by concd. HCl at 5–10°	5.0	3.9	Nil	Nil	4.5	19.2	Nil	Nil
Cold redn. of trimer (5–10°)	5.0	19.2	18.6	8.5	4.5	36.3	39.5	21.0
Hot redn. of trimer (70°)	5.0	21.1	1.8	0.4	...	..	...	..
Hydr. of amorphous higher polymer (5–10°)	4.0	3.7	..	..	2.4	30.8	...	..
Redn. of amorphous higher polymer (5–10°)	4.0	25.2	17.0	14.0	2.4	40.3	29.6	24.3

[a] Results for primary, secondary and tertiary amines obtained in reduction and hydrolysis experiments are corrected for the determined errors in the methods of separation. [b] Mixture contained 0.615 g. of aniline, 0.997 g. of methylaniline and 1.012 g. of dimethylaniline. [c] Mixture contained 0.987 g. of *p*-toluidine, 0.525 g. of methyl-*p*-toluidine and 0.564 g. of dimethyl-*p*-toluidine.

Ethylidene-dianiline was reduced by adding it in small portions to chilled concentrated hydrochloric acid, followed at once by zinc dust. The mixture of bases obtained by steam distillation was shaken in the cold with aqueous alkali and *p*-toluenesulfonyl chloride. The mixture was acidified, and the toluenesulfonyl derivatives extracted in ether. The aqueous liquid after suitable treatment was tested with picric acid; no diethylaniline was present. The ether solution of the mixed *p*-toluenesulfonyl derivatives was treated by the procedure outlined above for the benzenesulfonyl derivatives of *p*-toluidine and methyl-*p*-toluidine. After crystallization from alcohol the derivative of aniline melted at 102° (103.2° corr.) and that of ethylaniline at 87° (88° corr.).

The method used for the separation just outlined was tested semi-quantitatively with a mixture of 1.044 g. of aniline, 0.572 g. of ethylaniline, and 1.002 g. of diethylaniline. The recoveries were, respectively, 92.3, 84.4 and 104.1%.

Summary

1. Crystalline methylene-aniline and methylene-*p*-toluidine, prepared in very pure condition, were shown to be definitely trimeric at lower temperatures (5 to 80°), the average molecular weights decreasing at higher temperature (176°).

2. The method for the determination of the structures of polymerized Schiff bases by strong reduction, first used in the case of methylene-*p*-aminophenol, was successfully extended to trimeric methylene-aniline and methylene-*p*-toluidine, whose cleavage into primary, secondary and tertiary bases indicated their cyclic structures.

3. Amorphous methylene-aniline and methylene-*p*-toluidine (the higher polymers) were examined similarly and with similar results, but their structures cannot yet be fixed because of lack of knowledge of their molecular magnitudes at lower temperatures.

4. Examination of the apparently aberrant condensation of aniline and acetaldehyde (representing the straight-chain aliphatic aldehydes) showed the products hitherto obtained to be due to secondary reactions, the primary product being the di-imine. There seems to be no satisfactory evidence for the intermediate formation of the monomeric azomethine.